CHEMICAL ENERGETICS

1. Enthalpy change ΔH

- The total chemical energy inside a substance is called the enthalpy (or heat content)
- When chemical reactions take place, changes in chemical energy take place and therefore the enthalpy changes
- An enthalpy change is represented by the symbol Δ*H* (Δ= change; *H* = enthalpy)
- An enthalpy change can be positive or negative

Energy level diagrams

- An energy level diagram shows the energies of the reactants, the transition state(s) and the products of the reaction with time

- The **transition state** is a stage during the reaction at which chemical bonds are partially broken and formed

    - The transition state is very unstable – it cannot be isolated and is higher in energy than the reactants and products
    - The activation energy (E_a) is the energy needed to reach the transition state

- **Activation energy** is 'the minimum amount of energy needed for reactant molecules to have a successful collision and start the reaction'

Standard enthalpy changes

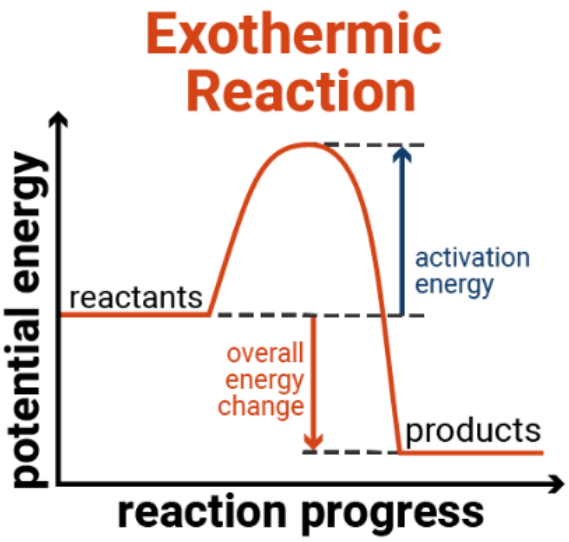
- The standard enthalpy change of reaction, is the enthalpy change when the amounts of reactants shown in the stoichiometric equation react to give products under standard conditions. The reactants and products must be in their standard states

- The standard enthalpy change of formation, is the enthalpy change when one mole of a compound is formed from its element under standard conditions. The reactant and products must be in their standard states.

- The standard enthalpy change of combustion, is the enthalpy change when one mole of a substance is burnt in excess oxygen under standard conditions. The reactants and products must be in their standard states.

- The standard enthalpy change of neutralisation, is the enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions

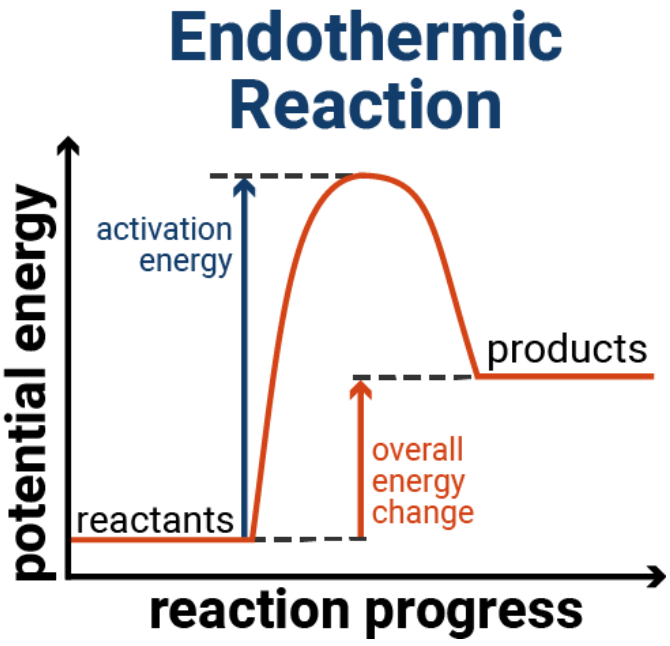
1.1 Exothermic reaction



- A reaction is exothermic when the products have less energy than the reactants
- Heat energy is given off by the reaction to the surroundings
    - The temperature of the environment increases - this can be measured on a thermometer
    - The temperature of the system decreases
- Bond forming - If more energy is released when new bonds are formed than energy is required to break bonds, the reaction is exothermic
- There is an enthalpy decrease during the reaction so ΔH is negative
- The reactants are therefore closer in energy to the transition state - exothermic reactions have a lower activation energy compared to endothermic reactions

1.2 Endothermic reaction

- A reaction is endothermic when the products have more energy than the reactants
- Heat energy is absorbed by the reaction from the surroundings
    - The temperature of the environment decreases - this can be measured with a thermometer
    - The temperature of the system increases
- Bond breaking - If more energy is required to break bonds than energy is released when new bonds are formed, the reaction is endothermic
- The reactants are therefore further away in energy to the transition state - endothermic reactions have a higher activation energy compared to exothermic reactions



1.3 Standard enthalpy change

- To fairly compare the changes in enthalpy between reactions, all reactions should be carried out under standard conditions

- These standard conditions are:
  - A **pressure** of 101 kPa
  - A **temperature** of 298 K (25 ◦C)
  - Each substance involved in the reaction is in its normal physical state (solid, gas or liquid)

- To show that a reaction has been carried out under standard conditions, the symbol ⊖ is used
  - $\Delta H^{\ominus}$ = the standard enthalpy change

Standard Enthalpy Change of ...	Definition	Symbol	Exothermic / Endothermic
Reaction	The enthalpy change when the reactants in the stoichiometric equation react to give the products under standard conditions.	$\Delta H°r$	Both
Formation	The enthalpy change when one mole of a compound is formed from its elements under standard conditions.	$\Delta H°f$	Both
Combustion	The enthalpy change when one mole of a substance is burnt in excess oxygen under standard conditions.	$\Delta H°c$	Exothermic
Neutralisation	The enthalpy change when one mole of water is formed by reacting an acid and alkali under standard conditions.	$\Delta H°neut$	Exothermic

One mole water is formed from hydrogen and oxygen, releasing 286 kJ of energy

$$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H_r^{\ominus} = -286\ kJ\ mol^{-1}$$

Calculate $\Delta H_r^{\ominus}$ for the reaction below:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Since two moles of water molecules are formed in the question above, the energy released is simply:

$\Delta H_r^{\ominus}$ = 2 mol x (-286 kJ mol^{-1})

= -572 kJ mol^{-1}

Calculate the $\Delta H_f^{\ominus}$ of the reaction below:

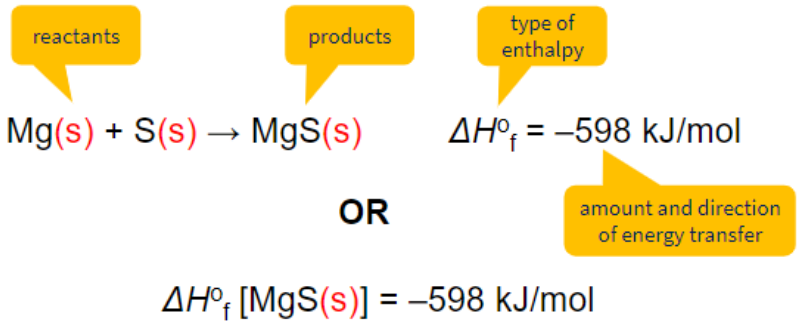
$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad \Delta H_f^{\ominus}[Fe_2O_3(s)] = -824.2\ kJ\ mol^{-1}$$

Since two moles of Fe_2O_3 (s) are formed the total change in enthalpy for the reaction above is:

$\Delta H_f^{\ominus}$ = 2 x (-824.2 kJ mol^{-1}) = - 1648 kJ

Enthalpy:

- Enthalpy, H is the total energy associated with the materials that react
- The total enthalpy of a system cannot be measured directly because the internal energy contains components that are unknown or not easily accessible
- Enthalpy changes happen during chemical reactions:
    - The total energy (enthalpy) of the reactant changes to form the final product
    - Enthalpy change is represented by the symbol ΔH



Enthalpy and bond energies

Exact bond energy

- The amount of energy required to break one mole of a specific covalent bond in the gas phase is known as exact bond energy or bond enthalpy (unit – KJ mol^{-1})
- The type of bond broken is put in brackets after E
    - Eg. E(H-H) is the bond energy of a mole of single bonds between two hydrogen atoms

Average bond energy

- Bond energies are affected by other atoms in the molecule (the environment)
- Therefore, an average of a number of the same type of bond but in different environments is calculated, this is called average bond energy

Measuring enthalpy changes:

- Enthalpy changes can be determined experimentally using the relationship:

$$\Delta H = -mc\Delta T/n$$

m = mass of liquid (g)

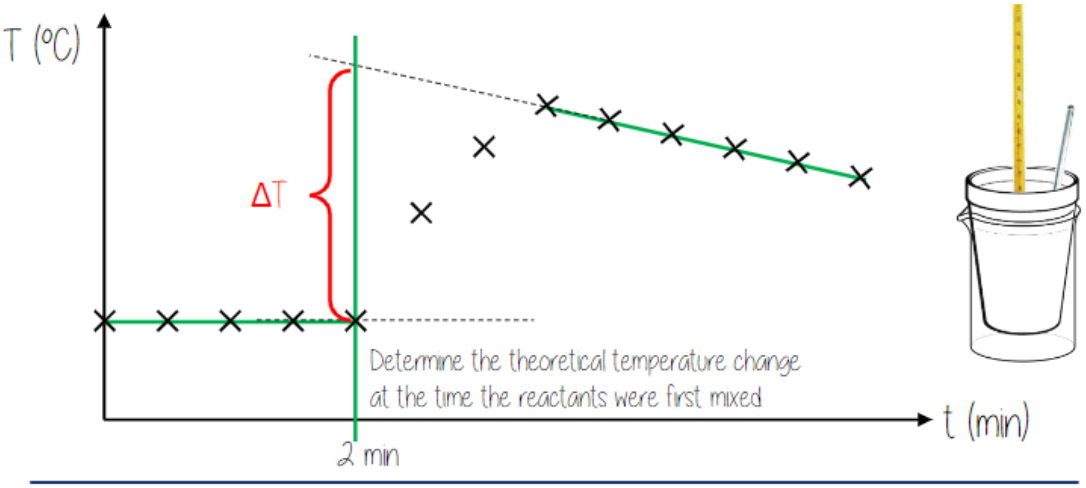
c = specific heat capacity (J g^{-1} $°C^{-1}$)

ΔT = temperature change (°C or K)

n = number of moles of limiting reactant

- Assumptions used when calculating enthalpy change:
    - The density of a solution = 1gcm^{-3} (=density of water)
    - The specific heat of a solution = 4.18 J g^{-1} °C^{-1} (=specific heat of water)
    - The reaction takes place under standard conditions and there is no heat lost to the surrounding

Extrapolation method (lab practical):



Standard enthalpy change of reaction:

- The enthalpy change when the amounts of reactants shown in the equation react to given products under standard conditions
    - The reactants and products must be in their standard states

$$MgCO_3(s) + HCl(aq) \rightarrow MgCl_2(s) + CO_2(g) + H_2O(l)$$

Standard enthalpy change of formation:

- The enthalpy change when on4edde mole of compound is formed from its elements under standard conditions
    - The $\Delta H^{\ominus}_f$ of any element in its most stable form at its standard state is zero

$Mg(s) + S(s) \rightarrow MgS(s)$ $\quad\quad$ $\Delta H^{\ominus}_f = -598$ kJ mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\quad\quad$ $\Delta H^{\ominus}_f = -285.8$ kJ mol^{-1}

Standard enthalpy change of combustion:

- The enthalpy change when one mole of substance is burnt in excess oxygen under standard conditions
- The products are always carbon dioxide (CO_2) and water (H_2O) for the combustion of organic compounds

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\quad \Delta H_c^{\ominus} = -882 \text{ kJ mol}^{-1}$

$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$ $\quad \Delta H_c^{\ominus} = -5644 \text{ kJ mol}^{-1}$

Standard enthalpy change of neutralization:

- The enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions
- In a common titration involving a monoprotic strong acid and base:

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\quad \Delta H^{o}_{neut} = -57 \text{ kJ mol}^{-1}$ (fixed value)

- If the reaction involves diprotic or triprotic acid with dibasic or tribasic base
  - $\Delta H_{neut} > -57 \text{ kJ mol}^{-1}$
- If the reaction involves weak acids and/ or weak bases
  - $\Delta H_{neut} < -57 \text{ kJ mol}^{-1}$
  - This is because the weak acid or weak bases undergo partial dissociation which reduces the concentration of H^+ ions in solution

Standard enthalpy change of atomization:

- The enthalpy change when one mole of gaseous atoms is formed from its element in its standard state under standard conditions

$Li(s) \rightarrow Li(g)$ $\quad \Delta H_{at}^{\ominus}[Li(s)] = +159.4 \text{ kJ mol}^{-1}$

$\frac{1}{2}F_2(g) \rightarrow F(g)$ $\quad \Delta H_{at}^{\ominus}[\frac{1}{2}F_2(g)] = +79 \text{ kJ mol}^{-1}$

$\frac{1}{2}I_2(s) \rightarrow I(g)$ $\quad \Delta H_{at}^{\ominus}[\frac{1}{2}I_2(s)] = +107 \text{ kJ mol}^{-1}$

- Bond energy:

  - …the energy required to break one mole of a bond in a gaseous molecule.

$F_2(g) \rightarrow 2F(g)$ $\quad E(F\text{-}F) = +158 \text{ kJ mol}^{-1}$

Relationship between BE and $\Delta H_{at}^{\ominus}$: $BE = 2\,\Delta H_{at}^{\ominus}$

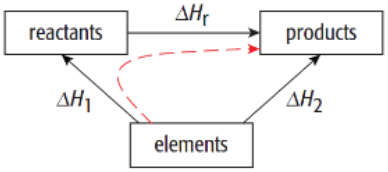
$\frac{1}{2}F_2(g) \rightarrow F(g)$ $\quad \Delta H_{at}^{\ominus}[\frac{1}{2}F_2(g)] = (+158/2) = +79 \text{ kJ mol}^{-1}$

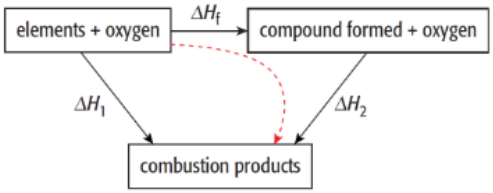
Hess's Law:

- Hess's Law states that 'the total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place' (as long as the initial and final condition are the same)
- Hess's Law is an application of:
    - Law of energy conservation – enthalpy change is the same no matter the number of steps taken
    - Law of mass conservation – no. of moles of atoms is the same throughout the cycle

Enthalpy cycles:

- Enthalpy cycles are used to illustrate Hess' Law





$\Delta H_2 = \Delta H_1 + \Delta H_r$

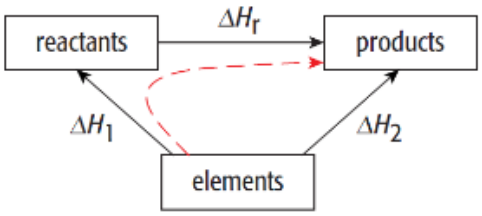
$\Delta H_r = -\Delta H_1 + \Delta H_2$

$\Delta H_1 = \Delta H_f + \Delta H_2$

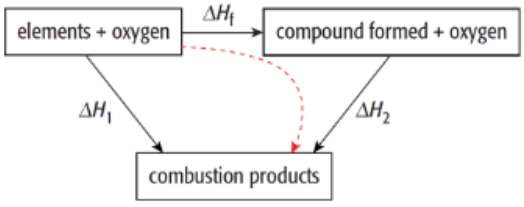
$\Delta H_f = \Delta H_1 - \Delta H_2$

Calculating enthalpy change:

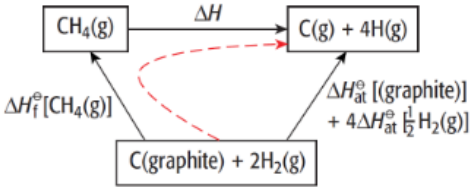
- **Enthalpy change of reaction from enthalpy changes of formation:**
    - Hess' Law can be used to calculate the enthalpy change of a reaction using the enthalpy changes of formation of the reactants and products
    - E.g. https://www.youtube.com/watch?v=V58fjITd_0I



- **Enthalpy change of formation from enthalpy changes of combustion:**
    - Hess' Law can be used to calculate the enthalpy change of formation of a compound using the enthalpy changes of combustion of the reactants and products



- **Enthalpy changes using bond energies:**
    - The enthalpy change of a reaction is the sum of the energy absorbed during bond breaking (endothermic reaction) and the energy released during bond forming (exothermic reaction)
    - $\Delta H_r = \Sigma(BE_{(reactants)}) - \Sigma(BE_{(products)})$
    - Average bond energy
        - Enthalpy cycle is necessary
        - E.g. average bond energy of the C-H bond in methane can be found using the ΔH_{at} of carbon and hydrogen and the ΔH_c or ΔH_f of methane.



Summary of equations:

1. $Q = mc\Delta T$
2. $\Delta H = -Q/n$

3. $\Delta H_r^\circ = \Sigma n(\Delta H_{f\ (products)}^\circ) - \Sigma m(\Delta H_{f\ (reactants)}^\circ)$
4. $\Delta H_r^\circ = \Sigma m(\Delta H_{c\ (reactants)}^\circ) - \Sigma n(\Delta H_{c\ (products)}^\circ)$
5. $\Delta H_r = \Sigma(BE_{(reactants)}) - \Sigma(BE_{(products)})$